Branched chain derivatives of alkyl oleates: Tribological, rheological, oxidation, and low temperature properties

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Abstract

We report the evaluation of four previously prepared oleochemical branched chain ethers (**1**–**4**) and soybean oil methyl esters (SME) against cloud point, pour point, oxidation stability, kinematic viscosity, specific gravity, lubricity, and surface tension. Ethers **1**–**4** exhibited excellent low temperature, oxidation stability, and lubricity behavior; however, at low blend levels (0.5, 1.0, 2.0 wt%) in SME, **1**–**4** had minimal impact on cloud point and pour point of SME. The specific gravity and surface tension behavior of **1**–**4** are nearly identical to SME. Ethers **1**–**4** displayed increased viscosity when compared to SME, but were still within ASTM D 6751 specifications at low blend levels in SME. Conversely, ethers **3** and **4** at 2.0% in SME were out of specification for kinematic viscosity in EN 14214. Both SME and **1**–**4** exhibited excellent tribological properties, as evidenced by HFRR wear scar behavior well within prescribed ASTM and CEN petrodiesel specifications.
Published by Elsevier Ltd.

Keywords: Additives; Biodiesel; Branched chain ethers

1. Introduction

Biodiesel (BD), an alternative fuel obtained from vegetable oils or animal fats, has a number of technical advantages over petrodiesel (PD), which include reduction of most exhaust emissions, improved lubricity and biodegradability, higher flash point, reduced toxicity, derivation from a renewable feedstock, and domestic origin [1–4]. In the case of viscosity, gross heat of combustion, and cetane number, BD and PD exhibit essentially similar behavior [1,2]. However, BD is inferior to PD when considering oxidation stability, nitrogen oxides (NO_x) emissions, energy content, and cold weather operability [4,5]. Strategies to improve one or more of the deficiencies of BD include the use of blends with PD, fractionation, feedstock modification, and the employment of additives [6]. The additive approach has attracted a great deal of interest; however, additives as developed for PD are generally ineffective when used in BD fuel [6–10]. Consequently, the development of effective additives for BD fuel is an important area of current research.

We report the evaluation of previously prepared [11,12] novel, oleochemical branched chain ethers (**1**–**4**, Fig. 1) against a number of relevant fuel parameters, such as cloud point (CP), pour point (PP), oxidation onset temperature (OT), signal maximum temperature (SMT), kinematic viscosity (υ), specific gravity (SG), lubricity (lub), and surface tension (γ). Further evaluation of the low temperature and viscosity properties of blends of **1**–**4** in soybean oil methyl esters (SME) will also be presented. A comparison of these results with relevant BD standards, such as ASTM D 6751 (Table 1) [13] and EN 14214 (Table 2) [14], will be included where applicable. The aim of this study is to aid in the development of bio-based materials for potential use as additives in biodiesel fuel (SME).

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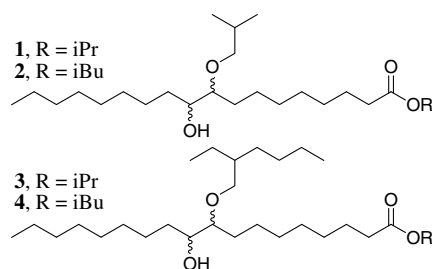 *E-mail address:* Bryan.Moser@ars.usda.gov (B.R. Moser).

Fig. 1. Synthetic branched chain ethers **1**–**4**. *Note*: *i*Pr = isopropyl; *i*Bu = isobutyl (2-methylpropyl).

Table 1
ASTM D 6751 standard specification for biodiesel fuel

Property	Test method	Limits	Units
Flash point (closed cup)	D 93	93.0 min	°C
Water and sediment	D 2709	0.050 max	% vol
Kinematic viscosity, 40 °C	D 445	1.9–6.0	mm^2/s
Sulfated ash	D 874	0.020 max	% mass
Sulfur	D 5453	0.0015 max (S15) 0.05 max (S500)	% mass
Copper strip corrosion	D 130	No. 3 max	–
Cetane number	D 613	47 min	–
Cloud point	D 2500	Report	°C
Carbon residue	D 4530	0.050 max	% mass
Acid value	D 664	0.50 max	mg KOH/g
Free glycerin	D 6584	0.020	% mass
Total glycerin	D 6584	0.240	% mass
Phosphorous content	D 4951	0.001 max	% mass
Calcium/magnesium	EN 14538	5 max, combined	ppm
Sodium/potassium	EN 14538	5 max, combined	ppm
Oxidation stability	EN 14112	3 min	h
Distillation temperature, atmospheric equivalent temp., 90% recovered	D 1160	360 max	°C
Alcohol control: one of the following must be satisfied			
1. Methanol content	EN 14110	0.2 max	% vol
2. Flash point	D 93	130.0 min	°C

Table 2
EN 14214 standard specification for biodiesel fuel

Property	Test method	Limits	Units
Ester content	EN 14103	96.5 min	% (mol/mol)
Density, 15 °C	EN ISO 3675, EN ISO 12185	860–900	kg/m^3
Kinematic viscosity, 40 °C	EN ISO 3104, ISO 3105	3.5–5.0	mm^2/s
Flash point	EN ISO 3679	120 min	°C
Sulfur content	EN ISO 20846, EN ISO 20884	10.0 max	mg/kg
Carbon residue (10% distillation residue)	EN ISO 10370	0.30 max	% (mol/mol)
Cetane number	EN ISO 5165	51 min	–
Sulfated ash	ISO 3987	0.02 max	% (mol/mol)
Water content	EN ISO 12937	500 max	mg/kg
Total contamination	EN 12662	24 max	mg/kg
Copper strip corrosion (3 h, 50 °C)	EN ISO 2160	1	degree of corrosion
Oxidation stability, 110 °C	EN 14112	6.0 min	h
Acid value	EN 14104	0.50 max	mg KOH/g
Iodine value	EN 14111	120 max	g I$_2$/100 g
Linolenic acid content	EN 14103	12.0 max	% (mol/mol)
Content of FAME with ⩾4 double bonds	–	1 max	% (mol/mol)
Methanol content	EN 14110	0.20 max	% (mol/mol)
MAG content	EN 14105	0.80 max	% (mol/mol)
DAG content	EN 14105	0.20 max	% (mol/mol)
TAG content	EN 14105	0.20 max	% (mol/mol)
Free glycerol	EN 14105, EN 14106	0.020 max	% (mol/mol)
Total glycerol	EN 14105	0.25 max	% (mol/mol)
Group I metals (Na, K)	EN 14108, EN 14109	5.0 max	mg/kg
Group II metals (Ca, Mg)	EN 14538	5.0 max	mg/kg
Phosphorous content	EN 14107	10.0 max	mg/kg

reported [11,12]. Blends of **1**–**4** (0.5, 1.0, and 2.0 wt%) in SME were prepared for analysis.

2. Experimental

2.1. Materials

Refined soybean oil (RSBO) was obtained from ADM Oils & Fats (Decatur, IL) and oleic acid (99%) from Nu-Chek Prep, Inc. (Elysian, MN). All other materials were obtained from Aldrich Chemical Company (Milwaukee, WI) and were used as received.

2.2. Synthesis of SME and branched chain ethers

Soybean oil methyl esters (SME) were prepared from RSBO and analyzed for quality as described previously [15,16]. The three-step synthesis of branched chain ethers **1**–**4** (Fig. 1) from oleic acid was accomplished as previously

2.3. Analytical methods

Cloud point (CP, °C) and pour point (PP, °C) determinations were made according to ASTM D 5773 [17] and D 5949 [18], respectively, using a Phase Technology Analyzer model PSA-70S (Richmond, B.C., Canada). Each sample was run in triplicate and average values rounded to the nearest whole degree are reported (Tables 3 and 4). For a greater degree of accuracy, PP measurements were done with a resolution of 1 °C instead of the specified 3 °C increment.

The PDSC (pressurized differential scanning calorimetry) experiments were performed using a DSC 2910 thermal analyzer from TA Instruments (Newcastle, DE). Typically, a 2 μL sample, resulting in a film thickness of <1mm, was placed in an aluminum pan hermetically sealed with a pinhole lid and oxidized in the presence of dry air (Gateway Airgas, St. Louis, MO), which was pressurized in the module at 1378.95 kPa (200 psi). A heating rate of 10 °C/min from 50 to 350 °C was used during each experiment. The

Table 3
Physical properties of branched chain ethers 1–4 and SME

	CP[a] (°C)	PP[a] (°C)	OT[a] (°C)	SMT[a] (°C)	υ^b (mm²/s)	SG[c]	Lub[d] (µm)	γ^e (mN/m)
1	−17	−21	203	336	12.64	0.88	144	28.4
2	−19	−22	198	333	15.01	0.89	139	30.1
3	−20	−23	196	315	40.62	0.89	142	26.9
4	−23	−25	195	314	57.98	0.93	139	27.1
SME	2	1	170	195	4.15	0.89	141	28.3

[a] $\sigma \pm 1\,°C$.
[b] $\sigma \pm 0.05\,mm^2/s$.
[c] $\sigma \pm 0.02$.
[d] $\sigma \pm 4\,\mu m$.
[e] $\sigma \pm 0.4\,mN/m$.

Table 4
Physical properties of a series of solutions (wt%) of 1–4 in SME[a]

	CP (°C)	PP (°C)	υ (mm²/s)
0.5% 1	1	0	4.17
1.0% 1	1	0	4.29
2.0% 1	0	−1	4.65
0.5% 2	2	0	4.22
1.0% 2	1	0	4.46
2.0% 2	0	−1	4.84
0.5% 3	1	0	4.18
1.0% 3	0	−1	4.73
2.0% 3	−1	−2	5.46
0.5% 4	1	0	4.46
1.0% 4	0	−1	4.89
2.0% 4	−1	−2	5.90

[a] See Table 3, footnotes a and b.

oxidation onset (OT, °C) and signal maximum temperatures (SMT, °C) were calculated from the resultant exotherm curve of each experiment. Each sample was run in duplicate and average values rounded to the nearest whole degree are reported (Table 3).

Kinematic viscosity (υ, mm²/s, 40 °C) and specific gravity (SG, 40 °C) were determined following ASTM D 7042 [19] using an Anton Paar Stabinger Viscometer model SVM3000 (Ashland, VA). Each sample was run in triplicate and average values are reported (Tables 3 and 4).

Lubricity determinations were made at 60 °C (controlled to less than ±1 °C), according to ASTM D 6079 [20] using a PCS Instruments (London, UK) Model HFRHCA8 High Frequency Reciprocating Rig (HFRR) lubricity tester. At the conclusion of each test the ball was visually inspected for wear and the dimensions of an observed wear scar (µm) on the ball were averaged. All wear scar data (Table 3) are the averages of two replicates.

Surface tension (γ, mN/m) measurements were conducted at room temperature with a Kibron (Helsinki, Finland) Microtrough X instrument running in tensiometry mode using Filmware 3.57 software. A model 6206 300 µL multi-well Teflon and glass plate and a model 6002 wire probe were utilized. Each sample was run in triplicate and average values are reported (Table 3).

3. Results and discussion

3.1. Low temperature behavior

Each of the four synthetic branched chain ethers (1–4, Fig. 1) exhibited superior low temperature performance when compared to SME, as determined by CP and PP. Furthermore, 2-ethylhexyl ethers 3 and 4 have superior cold flow properties when compared to isobutyl ethers 1 and 2 (Table 3). Such a result is expected, since bulkier substituents (2-ethylhexyl ethers) are more likely to impede macrocrystalline formation at low temperatures than their less bulky counterparts (isobutyl ethers) by more effectively disrupting the arrangement of molecules into an orderly pattern. A similar trend was observed when comparing isopropyl ester 1 to isobutyl ester 2 and, analogously, 3 to 4. The substance that afforded the most favorable cold flow behavior was 2-ethylhexyl ether 4 (CP −23 °C; PP −25 °C; Table 3), which contained the most bulky ether (2-ethylhexyl) and ester (isobutyl) moieties evaluated in this study.

A series of solutions (0.5, 1.0, and 2.0 wt%) of 1–4 in SME was evaluated against both CP and PP in an effort to measure the influence of branched chain ethers on the cold weather operability of SME. In general, 3 and 4 were more effective than 1 and 2 at lowering CP and PP of blends with SME. No improvement in CP and PP of SME was detected at blend levels lower than 0.5 wt% (data not shown), but as the blend level of 1–4 in SME was increased, a corresponding reduction in CP and PP was observed (Table 4). However, only modest reduction in CP and PP of SME was achieved, even at relatively high (2.0 wt%) additive levels. For instance, 2.0 wt% of 2-ethylhexyl ether 4 in SME yielded a marginal improvement in CP and PP (CP −1 °C; PP −2 °C; Table 4) over that of unblended SME (CP 2 °C; PP 1 °C; Table 3).

3.2. Viscosity

Both ASTM D 6751 (Table 1) and EN 14214 (Table 2) contain specifications for kinematic viscosity (υ, 40 °C). Hence, viscosity was measured for SME, 1–4, and blends of 1–4 in SME. The synthetic branched ethers 1–4 were significantly more viscous than SME. In fact, a pattern was elucidated whereupon υ increased as the level of steric bulk increased, which yielded a trend of 4 (most bulky synthetic adduct, 57.98 mm²/s) > 3 >> 2 > 1 (least bulky, 12.64 mm²/s) >> SME (4.15 mm²/s, Table 3). Consequently, a strong correlation between the ability of branched chain ethers to inhibit macrocrystalline formation and kinematic viscosity was detected. In other words, as CP and PP of branched chain ethers was lowered, a corresponding increase in υ was noticed. Despite the increase in υ observed for ethers 1–4 in comparison to SME, 1 and 2 were still less viscous than soybean oil (SBO, 32.6 mm²/s at 40 °C) [21]. Of course a major reason for the use of SME instead of SBO as an alternative fuel is that υ of

SME is much closer to PD (2.70 mm^2/s for No. 2 PD at 40 °C) than SBO [6,21,22].

All of the branched chain ethers (**1**–**4**) were out of specification for υ in both ASTM D 6751 and EN 14214, especially 2-ethylhexyl ethers **3** (40.62 mm^2/s) and **4** (57.98 mm^2/s). With respect to blends of **1**–**4** in SME, all were within the prescribed ASTM D 6751 kinematic viscosity range; however, 2.0% **3** (5.46 mm^2/s) and 2.0% **4** (5.90 mm^2/s) in SME were out of specification for EN 14214 (Table 4).

Although not a specification in either ASTM D 6751 or EN 14214, specific gravity (SG) is often used as a tool in determining the quality of fuels and other liquid substances. Therefore, SG (40 °C) was measured and **1**–**4** (0.88–0.93) were similar to SME (0.89, Table 3). Additionally, blends of **1**–**4** in SME showed essentially no change in SG (results not shown) with respect to neat SME.

3.3. Oxidation stability

Oxidation stability is a critically important fuel characteristic, as oxidative degradation can adversely affect kinematic viscosity and acid value, both of which are specified in ASTM D 6751 and EN 14214. As such, EN 14214 contains an oxidation stability parameter of a minimum of 6 h at 110 °C, as determined by the Rancimat method (EN 14112). Conversely, ASTM D 6751 requires that a sample remain stable for at least 3 h at 110 °C as determined by the Rancimat method. Recent work has established pressurized differential scanning calorimetry (PDSC) as a potential alternative to Rancimat and OSI methods as an analytical tool for the accelerated evaluation of oxidation stability of BD and other oleochemicals [23]. Therefore, the oxidation onset (OT, °C) and signal maximum temperatures (SMT, °C) of SME and ethers **1**–**4** were determined by PDSC. Ethers **1**–**4** exhibited OT and SMT significantly higher than SME (Table 3), which is an indication of greater oxidation stability. This is probably due to the absence in **1**–**4** of characteristically susceptible allylic and bis-allylic methylene positions found along the fatty acid backbone of typical BD, making **1**–**4** less vulnerable to oxidation. However, **1**–**4** are not expected to participate in any of the mechanisms of oxidation inhibition, as they do not contain any of the classic functionality required for such activity, such as conjugated polyene systems (e.g., carotenoids, lycopene, etc.), quinone groups (TBHQ, etc.), or polyphenolic functionality (gallates, resveratrol, etc.). Hence, further oxidation stability studies, such as Rancimat, were deemed unnecessary since any increase in oxidation stability of the blends, if any, would be due to a blending effect and not genuine antioxidant behavior attributable to **1**–**4**.

3.4. Tribology

Both ASTM D 6751 and EN 14214 do not contain lubricity requirements since BD possesses inherently good lubricity; however, it is a critical fuel property. Fuels with poor lubricity can cause failure of diesel engine parts that rely on lubrication by the fuel, such as fuel pumps and injectors [6,24]. As such, lubricity specifications are included in PD standards in the USA (ASTM D 975) and EU (EN 590). The specified maximum allowable wear scars by HFRR are 460 μm (60 °C) in EN 590 [25] and 520 μm (60 °C) in ASTM D 975 [26]. However, a recent study indicated that fuels with wear scars greater than 460 μm (60 °C) may not possess sufficient lubricity for practical long term use in diesel engines [27]. It is widely known that BD (SME: 141 μm, Table 3) has vastly superior lubricity to PD (ULSD: 651 μm) by HFRR [28]. In fact, because of this reason many governmental organizations have passed or are considering regulations requiring the use of 2–5% BD in ULSD. Additionally, ethers **1**–**4** (139–144 μm, Table 3) exhibited wear scar behavior essentially equivalent to SME. Hence, blends of **1**–**4** in SME were not evaluated with respect to lubricity. Perhaps **1**–**4**, like SME, may serve as effective lubricity additives for ULSD.

3.5. Surface tension

Although surface tension (γ) is not specified in either ASTM D 6751 or EN 14214, it is nevertheless an important fuel combustion property, as it is implicated in the atomization process [29,30]. Hence, γ of ethers **1**–**4** was measured and compared to SME. As can be seen from Table 3, γ of **1**–**4** was similar to SME, as were blends of **1**–**4** in SME (results not shown).

4. Conclusions

Each of four synthetic oleochemical branched chain ethers (**1**–**4**) was evaluated against a number of important BD fuel parameters and compared to SME. All of the branched chain ethers exhibited excellent low temperature performance, oxidation stability, and lubricity behavior. However, at low blend levels in SME the materials had minimal impact on CP and PP. Specific gravity, surface tension, and lubricity of **1**–**4** were nearly identical to SME. Ethers **1**–**4** display increased viscosity when compared to SME, but were still within ASTM D 6751 specifications at low blend levels in SME. Conversely, ethers **3** and **4** at 2.0% in SME were out of specification for kinematic viscosity with regard to EN 14214. A strong correlation between the ability of branched chain ethers to inhibit macrocrystalline formation and increased kinematic viscosity was also detected. SME and **1**–**4** exhibited essentially equivalent HFRR wear scar behavior that was well within PD specifications. In conclusion, branched chain ether **1**–**4** may aid in the development of bio-based materials for potential use as additives in biodiesel fuel (SME). With continued chemical modification, a useful lipid-derived BD additive may soon result.

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Acknowledgement

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